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# Global-scale evidence for the refractory nature of riverine black carbon

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Abstract: Wildfires and incomplete combustion of fossil fuel produce large amounts of black carbon. Black carbon production and transport are essential components of the carbon cycle. Constraining estimates of black carbon exported from land to ocean is critical, given ongoing changes in land use and climate, which affect fire occurrence and black carbon dynamics. Here, we present an inventory of the concentration and radiocarbon content ($\Delta$ 14C) of particulate black carbon for 18 rivers around the globe. We find that particulate black carbon accounts for about 15.8 $\pm$ 0.9% of river particulate organic carbon, and that fluxes of particulate black carbon co-vary with river-suspended sediment, indicating that particulate black carbon export is primarily controlled by erosion. River particulate black carbon is not exclusively from modern sources but is also aged in intermediate terrestrial carbon pools in several high-latitude rivers, with ages of up to 17,000 14C years. The flux-weighted 14C average age of particulate black carbon exported to oceans is 3,700 $\pm$ 400 14C years. We estimate that the annual global flux of particulate black carbon to the ocean is 0.017 to 0.037 Pg, accounting for 4 to 32% of the annually produced black carbon. When buried in marine sediments, particulate black carbon is sequestered to form a long-term sink for CO2.

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# Global scale evidence for the refractory nature of riverine black carbon

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Wildfires and fossil fuel incomplete combustion produce large amounts of black carbon. Black carbon production and transport are essential components of the carbon cycle. Constraining estimates of black carbon exported from land to ocean is critical, given on-going changes in land use and climate, which affect fire occurrence and black carbon dynamics. Here, we present an inventory of the concentration and radiocarbon contents ($\Delta^{14}C$) of particulate black carbon for 18 rivers around the globe. We find that particulate black carbon accounts for about 15.8±0.9% of river particulate organic carbon, and that fluxes of particulate black carbon co-vary with river suspended sediment, indicating that particulate black carbon export is primarily controlled by erosion. River particulate black carbon is not exclusively from modern sources but is also aged in intermediate terrestrial carbon pools in several high latitude rivers, with ages of up to 17,000 $^{14}C$ yrs. The flux-weighted $^{14}C$ average age of particulate black carbon exported to oceans is 3700 years. We estimate that the annual global flux of particulate black carbon to the ocean is 0.017 to 0.037 Pg, accounting for 4 to 32% of the annually produced black carbon. When buried in marine sediments, particulate black carbon is sequestered to form a long-term sink for $CO_2$.

Forest fires and fossil fuel combustion release large amounts of carbon as greenhouse gases and aerosols into the atmosphere, contributing to the on-going changes in Earth's climate that are occurring at an unprecedented rate [1]. Up to 27% of this fire-derived carbon is transformed into Black Carbon (BC, or pyrogenic carbon, charcoal residues [2]) – a byproduct of incomplete combustion - rather than emitted as greenhouse gases [3]. The majority of BC is from vegetation fires (Figure 1). Once incorporated into surface reservoirs (e.g. soils, lake sediments), BC participates in many biogeochemical processes, and influences carbon cycling on local to global

scales [3,4]. Biomass burning transfers carbon from fast-cycling (atmosphere-biosphere) pools to more slowly cycling soil and sedimentary reservoirs [5], creating a long-term carbon sink [6,7]. Due to its aromatic structure, a substantial fraction of BC decomposes slowly [8,9], and can persist in soils for hundreds to thousands of years [5,10].

Greater understanding of the role of this slow-cycling component of the carbon cycle and its significance as a sink of atmospheric $CO_2$ requires improved constraints on the origin, dynamics and fate of BC. River systems connect terrestrial and marine carbon cycles, exporting approximately 2.7 Pg C $yr^{-1}$ to the oceans [11], where it is ultimately either mineralized to $CO_2$ and $CH_4$ [12-14] or sequestered in sediments [15]. Rivers deliver BC from land to the ocean both as particulate BC (PBC) in particulate organic carbon (1<63 µm) and dissolved BC (DBC) in dissolved organic carbon (<1 µm)[4,16]. Dissolved BC, which comprises a substantial fraction (10%) of dissolved organic carbon (OC) globally, is continuously exported from soils for decades after wildfire burning [17,18] (26.5 Tg $yr^{-1}$), and can cycle in the deep ocean on millennial timescales (~ 20,000 $^{14}C$ yrs) [19,20]. The global amount and age of PBC transported by rivers, on the other hand, has remained largely unknown until now. PBC river fluxes, age and transport are essential for constraining land-ocean transfer as well as assessing its significance as a $CO_2$ sink by sequestration in continental margin sediments [21]. Current global PBC flux estimates vary by a factor of 20 (0.005-0.108 Pg $yr^{-1}$) [22,23], and the magnitude and timescales of transport, transformation and degradation processes are not well understood [16,24]. As river basins are facing anthropogenic pressures, both directly via changes to the land surface (e.g. increasing fire intensity and frequency, accelerated deforestation, conversion to agriculture) and fluvial networks (e.g. dams, channelization, irrigation), and indirectly via climate change (e.g. increasing

74 temperatures and an invigorated hydrological cycle) [11,25,26], we need to better
75 constrain PBC river export for assessing past and future perturbations of this slowly
76 cycling pool in the carbon cycle.
77
78 Here, we use the abundance and radiocarbon ($^{14}C$) content to constrain the flux and
79 age of river PBC of 18 globally distributed rivers. We quantify river PBC in suspended
80 or deposited sediments collected at the terminus of 11 of the largest rivers worldwide,
81 (such as the Amazon, Congo, Brahmaputra, and major Arctic rivers) and 7 small
82 mountainous rivers [27] (S.Table 1). These samples represent 15-34% of the global
83 organic carbon exported by rivers (high and low estimates of export[28]). We used river
84 suspended sediments (collected by filtration) or freshly deposited river sediments (<63
85 µm) (Supplementary Materials, S.Figure 1). We measured BC in Particulate Organic
86 Carbon (POC, as <63um size fraction), providing the age of PBC at or near the river
87 terminus (S.Table 1, S.Figure 1). To characterize PBC derived predominantly from
88 residues of biomass burning, we use chemical oxidation to liberate corresponding
89 benzene polycarboxylic acids (BPCAs) [29]. The analytical window captured by this
90 method implies that the mass weighted PBC fluxes are conservative under-estimates
91 for PBC fluxes, since it does not include by-products of low-temperature fires (e.g.
92 levoglucosan [21,30]). We assume BC molecular markers have the same $^{14}C$ age within
93 BC. Subsequently, we purified BPCA marker compounds [29] and converted them to
94 $CO_2$ followed by $^{14}C$ measurement by gas ion source Accelerator Mass Spectrometry
95 [31]. PBC fluxes from each river were estimated by multiplying the relative PBC
96 concentration (from BPCA concentrations) with the reported biospheric OC yield of
97 each river[28], thereby normalizing PBC to biospheric OC export. The biospheric OC
98 yield was calculated using previous reported data and linear correlations between

biospheric OC yield and sediment yield[28] (Supplementary Information).

**Black carbon is a major component of river organic carbon**

We find PBC comprises a significant component of river POC (15.8±0.9% PBC river flux-weighted mean, n=18, Supplementary Materials). This proportion of river PBC is similar to global averages of the riverine dissolved BC (10.6±0.7%) [18] and of soil organic carbon (13.7%) [32]. The proportion of PBC as a component of river POC ranges from 2.7±0.4 % PBC (Pettaquamscutt) to 32.9±2.9 % PBC (Eel) (Supplementary Materials, S.Table 2, S.Figure 2). Corresponding PBC fluxes from rivers range from 8±2 (Fraser) to 1162±218 Gg $yr^{-1}$ (Amazon). There is no correlation between BC concentration and river basin drainage size (S.Figure 3), however PBC yield is positively correlated with suspended sediment yield (sediment discharge normalized to the drainage area). This correlation follows a power-law relationship ($r^2$=0.64) (Figure 3a) indicating that the rate of PBC export is controlled primarily through soil erosion, mobilization and transport processes, much like export of POC [28,33]. PBC concentrations vary by a half order of magnitude, while suspended sediment yield varies by four orders of magnitude, illustrating that PBC export is primarily controlled by erosion (not concentration). Given that rivers sequester the majority of terrestrial exported POC by burial in ocean sediments [34], these observations establish a direct link between soil erosion and PBC sequestration on continental margins.

**Time lags between black carbon production and river export**

We find a large range in PBC $\Delta^{14}C$ values, indicating fast (+74±62 ‰, modern, Congo) to slow (-880±12‰, 17,000±780 $^{14}C$ yrs, Colville) PBC cycling within individual

123 watersheds (Figure 3, S. Table 1). The global flux-weighted age average of 3,700±400
124 $^{14}$C yrs (-372±28‰) is significantly higher (older) than the few measurements of river
125 dissolved BC (450±280 $^{14}$C yrs, 475±150 $^{14}$C yrs and 1140 $^{14}$C yrs, from [16,19,20]).
126 Globally, PBC is older than total POC, with two exceptions in the Godavari and Congo
127 Rivers where PBC is modern (Figure 3). Assuming all BC produced from burning of
128 modern biomass has a mean post-bomb $\Delta^{14}$C value of +100‰ and BC derived from
129 fossil fuel combustion has a $\Delta^{14}$C value of -1000‰ (i.e., is radiocarbon-depleted), we
130 estimate that 44±28% of river PBC is from fossil fuel contributions (Supplementary
131 Materials). However, assuming only two end members is too simplistic given the range
132 of potential PBC sources and transport pathways [16,35]. A regional study in the
133 Pettaquamscutt River basin (USA) estimated a maximum fossil fuel BC contribution of
134 only 19%, and indicated that there is a time lag between production and river export
135 of PBC[35]. This implies that BC can "pre-age" during temporary storage in intermediate
136 terrestrial reservoirs such as soils[35].
137
138 River PBC thus reflects at least three pools: i) biomass-derived char from recent
139 vegetation fires, ii) pre-aged BC (held within the catchment in soils, wetlands and
140 floodplains before river transport and ocean deposition [35]), and iii) fossil fuel-derived
141 BC. Fossil fuel-derived BC mass contributions are considered minor for the following
142 reasons. First, the annual production of biomass-derived BC (114-383 Tg yr$^{-1}$) is one
143 to two orders of magnitude higher than BC produced by fossil fuel combustion (2-29
144 Tg yr$^{-1}$) (Figure 1). Second, soil formation rates span centuries to millennia, and the
145 vast majority of BC eroded from soils must pre-date the beginning of the industrial
146 revolution. Third, there is mounting evidence that soil OC inputs dominate the POC
147 load in most river systems [28,36], as indicated for PBC by our own data. PBC

148 contributions to river PBC pools are therefore likely dominated by inputs from biomass
149 burning.
150
151 Given the importance of soil OC as a component of riverine POC export, rivers
152 constitute a source of pre-aged PBC. PBC can be temporarily stored in soils and
153 alluvial deposits for thousands of years [37,38], much like other molecular markers of
154 terrestrial vegetation (e.g., higher plant-derived long-chain *n*-alkanes and *n*-alkanoic
155 acids) [39-41]. River PBC $^{14}C$ ages are generally higher (older) than those of other
156 terrestrial vegetation molecular markers [39-41] implying slower PBC turnover rates.
157 Moreover, the correlation between $\Delta^{14}C$ values of PBC and POC (Figure 3b, $r^2$=0.48,
158 p=0.005) suggests that pre-aged soil OC, including PBC, is an important component
159 of overall OC export. This linear relationship is close to unity (1.05±0.02), indicating
160 that common mechanisms are responsible for aging of both soil OC and BC pools, as
161 well as implying that the ratio of BC and non-BC reactivity is roughly constant,
162 regardless of environmental conditions. PBC experiences pre-aging (relative to POC)
163 in river basins by a relatively constant amount globally, including locations where
164 environmental conditions both favor preservation or mineralization.
165
166 **Global implications and future outlook**
167 Although sequestration in marine sediments is considered to be the ultimate fate of
168 BC [21] (Figure 1), marine sediment BC burial fluxes only account for 3-10% of global
169 BC production fluxes [42]. In soils, BC constitutes on average 13.7% (ranging to 50%)
170 of total organic carbon [32]. This inconsistency between BC in soils and marine
171 sediments raises the question as to where the majority of BC produced annually on
172 land goes. Inland waters are both significant holding pools of organic carbon (with

storage of up to 50% of carbon along the river-to-ocean continuum), and processers of this carbon [12,14,43]. In this way, PBC may be sequestered for years up to millennia in intermediate reservoirs prior to export and burial in marine sediments [35,44]. For example, PBC has been found to be retained in alluvial deposits for thousands of years [37], implying that BC can undergo pre-aging en-route to its ultimate burial site. The large fluxes and diverse ages of PBC in our study supports the conclusion that dissolved and particulate BC pools in rivers are partially decoupled, with dissolved BC driven by hydrology [16,19,45] whereas PBC is subject to erosional and depositional dynamics (Figure 1). This preliminary global assessment of river PBC flux represents an underestimate since it is based on BPCA markers tracing the most refractory components of BC (i.e., it does not include more labile BC from low temperature fires [30]). Our study highlights the need for further source-to-sink studies to determine controls on the fluxes and degrees of pre-aging of PBC in river catchments prior to export.

Assuming a soil BC stock of 200 Pg [32], and a BC production rate of 0.123-0.56 Pg C per yr , the BC mean turnover time in soils at steady state ranges from 1600 to 3500 yrs (Figure 1) [4]. This is much longer than estimates of bulk soil OC turnover times (mean residence time, 25-110 yrs) [46], highlighting the refractory nature of BC, and consistent with our estimated watershed-wide erosion rates. Using our weighted mean PBC as a fraction of biospheric POC (15.8±0.9%) and estimated global biospheric POC flux ($0.157^{+74}_{-50}$ Pg yr$^{-1}$ [28]), we estimate an annual global flux of PBC to the ocean of 0.017-0.037 Pg BC. This riverine PBC flux is approximately equal to the global dissolved BC flux (0.027 Pg yr$^{-1}$)[18] indicating that, relative to atmospheric fluxes (0.002-0.005 Pg yr$^{-1}$)[4], river transport serves as the dominant process for mobilization

198 of BC from land to ocean (Figure 1). Thus, rivers transport 4-32% of the 0.114-0.383
199 Pg BC that is produced annually to the oceans. This is one to two orders of magnitude
200 larger than the fraction of biospheric OC that is exported, indicating that a much larger
201 fraction of PBC (relative to biospheric OC or dissolved BC) is laterally exported instead
202 of respired in soils. Furthermore, the average age of riverine PBC (3,700±400 $^{14}$C yrs)
203 is closer to the calculated mean BC turnover time (800-1000 yrs) [47] in soils than that
204 of the biospheric OC (~50 yrs)[48]. Together these observations provide global evidence
205 that PBC is more refractory than POC. Like POC [49], river PBC is likely to be transferred
206 and buried in marine sediments on continental margins, and thus preserved over
207 geological timescales. Indeed, our estimated global riverine PBC flux amounts to 20%
208 of the terrestrial organic carbon stored annually in ocean sediments [50], suggesting that
209 processes of BC production, protracted storage in terrestrial reservoirs, mobilization
210 and burial in marine sediments thus represent an important geologic $CO_2$ sink.
211
212 These findings have implications for our understanding of the role of BC cycling in the
213 face of direct (e.g., land-use) and indirect (climate) anthropogenically-driven change.
214 Some increases in the intensity and frequency of fires with on-going climate change
215 [51,52] may enhance BC production. Here, we find river PBC is efficiently exported and
216 stored in sediments rather than degraded to $CO_2$ en-route to burial in the ocean,
217 suggesting a negative feedback to increased biomass burning. Such interpretations
218 are likely overly simplistic, by not taking into account seasonal differences between
219 production and erosion of BC. However, the strong correlations imply that these
220 trends are robust at a global scale. Nevertheless, it is clear that further consideration
221 of BC dynamics within river basins at regional and global scales is warranted in order
222 to better constrain this important component of the carbon cycle.

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445

446 **Author contributions**

447 D.W., T.E., M.S, and A.C. contributed to the design of the study. River samples were
448 provided by T.E., G.N, M.U., T.B., C.F., E.S., M.Z., B.V., V.G., M.R. and B.P.E.
449 A.C. and D.W. conducted the black carbon laboratory analyses. N.H., A.C., U.H, and
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451 measurements. V.G., A.C., S.A, M.S., E.S. and T.E. contributed to data analysis and
452 interpretation. A.C. authored the manuscript and built the figures. All authors
453 contributed comments and input on this manuscript.

454

455 **Financial and non-financial competing interests**

456 The authors declare no competing financial interests.

457

458 **Data availability**

459 We included our global river BC concentration, BPCA relative abundance, flux and
460 $F^{14}C$ river data set on the PANGAEA data (www.pangaea.de) repository following

461 publication under the username alyshacoppola, (connected to the ORCIDID
462 https://orcid.org/0000-0002-9928-2786). Available information on data sources for
463 catchment size, sediment yield and biospheric POC are from SI Table 1 in Galy et al.,
464 (2015)
465 (http://www.nature.com/nature/journal/v521/n7551/abs/nature14400.html#supplementary-information).
466 tary-information). In addition, all data is available from corresponding author on
467 request.
468
469 **Figure captions**
470
471 Figure 1. **Global schematic synthesis of the BC cycle in major reservoirs**.
472 Estimates are derived from Supplementary Table 3. The relative size of the reservoir
473 (Tg) is given by the size of the circle. Schematic BC $\Delta^{14}C$ values are given by the
474 shade of white (modern, post 1950) to dark red (ancient -1000‰) in (circle) reservoirs
475 and river BC (arrow) pools. Fluxes are in Tg $yr^{-1}$ given by the relative size of the blue
476 and red arrows.
477
478 Figure 2. **Range of river PBC fluxes (Gg $yr^{-1}$) and PBC $\Delta^{14}C$ values (‰) of**
479 **particulate black carbon in rivers distributed globally**. PBC $\Delta^{14}C$ values are given
480 by the shade of yellow (bomb) to dark red (ancient -1000‰) for the river catchment.
481 Rivers were sampled at their outlets. Small colored circles indicate small mountainous
482 rivers with drainage basin areas less than 250,000 $km^2$. The histogram represents
483 fluxes per river (Gg $yr^{-1}$), where the grey bar represents the flux of the Padma, which
484 is the combined fluxes of the Brahmaputra and Ganges rivers.
485

Figure 3. a) **The relationships between particulate black carbon yield and suspended sediment yield indicates that export is controlled by erosion.** PBC was normalized to the biospheric OC yield given in [28]. The regression line is $Y_{PBC\ yield} = 0.005(Y_{sed})^{0.72}$ ; $r^2$=0.64; P<0.001. b) Relationship between $\Delta^{14}C$ values of PBC and POC. The regression line is $Y_{PBC14C} = 0.96(X_{biosphericOC})-151$ ; $r^2$=0.48; P<0.0125.

## Methods

### Study sites and sample collection

We studied 18 river systems. Sampling was not intended to resolve seasonal, climate or vegetation features but to provide a first order assessment of the content, $\Delta^{14}C$ values and structure of river PBC exported. These samples include 11 of the largest rivers worldwide, such as the Amazon, Congo, Brahmaputra, and major Arctic rivers. We included samples from small rivers and rivers through mountainous regions because they export a high sediment load, despite their relatively low discharge [53,54]. We used samples that were well characterized in previous studies (Supplementary Table 1).

Four types of river samples were used, including river bed sediments, flood plain river deposits, shelf deposits and suspended river bank material. River bed sediments were collected at the apex of the river using a Van Veen grab sampler. Flood plain river sediments were deposited during decreasing water level of the last high water event and expected to represent an average composition of POC during the time of deposition[55]. River sediments were collected from the flanks of the river at the apex of the delta. River and flood plain sediments are defined as recently accumulated sediment from the riverbank or in very calm or shallow water deposited

511 during lower water levels following the last high water event (Supplementary Figure
512 1). Shelf deposits were collected on the continental margins using a piston corer
513 (system built in-house at Geology and Geophysics, Woods Hole Oceanographic
514 Institution (WHOI), core diameter 2 and 3 inch). Suspended river bank material was
515 collected on GF/F glass fiber filters. Bulk river sediments were wet sieved with Milli-
516 Q water over 200 µm and 63 µm sieves on a shaking table in order to remove coarse
517 particles and organic debris. The resulting <63 µm fraction was kept frozen and
518 freeze-dried until BC analysis.
519
520 **Particulate black carbon content and quality**
521 PBC was extracted from the POC (<63 µm, no lower limit) samples using the BPCA
522 (benzene polycarboxylic acid) method [29,55]. Hydrofluoric acid (HF, 10% Sigma Aldrich
523 7664-39-4) was used to demineralize interfering materials for PBC $\Delta^{14}C$ analysis.
524 Environmental clay and silica matrices of POC interfere with BC analysis of low OC%
525 samples. Following Schmidt et al., [58] carbonates and salts were first dissolved in 1N
526 HCl for 24 hours at room temperature. The residue was separated by centrifugation
527 and rinsed with Milli-Q water. Silicate minerals were then removed using treatments
528 of 10ml of 10% HF, added to 5 g aliquots of POC. Samples were shaken at room
529 temperature, centrifuged and the supernatant was removed. The procedure was
530 repeated 5 times, then rinsed 10 times with Milli-Q water to remove salts, residual HF
531 and to neutralize the sample. Samples were then dried. Concentrated nitric acid was
532 added to the sample in a quartz pressure digestion chamber at 170°C for 8 hours to
533 produce BPCAs. After digestion, the solution was filtered, run through a cation
534 exchange column (DOWEX 50WX8), lyophilized, further cleaned with a solid phase
535 extraction (Discovery DSC-18), and re-dissolved in Milli-Q.

BPCAs were separated and collected on a preparative liquid chromatography using an Agilent 1290 infinity HPLC system equipped with a 2.7 µm Agilent Poroshell 120 C-18 column. A reverse phase analytical C-18 column (Agilent, 2.7µm) was used with two mobile phases of pH 2 Milli-Q (1.7% $H_3PO_4$) and acetonitrile (>99.98% Scharlau, $F^{14}C$ <0.004). Quantification of BPCAs were made from seven-point calibration curves (2 to 200 ng µL−1) using commercially available BPCA standards including pentacarboxylic acid (Aldrich S437107) and hexacarboxylic acid (Aldrich M2705) to quantify the BPCAs measured from peak areas obtained from the diode array detector (60 mm path length) chromatographs. A BC recovery factor of 23.2±0.4% was used for the conversation of BPCAs to estimate BC [56,57] for comparison with published values. For $\Delta^{14}C$ analysis, B5CA and B6CA marker compounds were collected in the fraction collector of the HPLC, according to the method in Wiedemeier et al., (2016) . We assume that all BPCA molecular markers have the same age within BC. The B2CA marker compounds were not collected, because may also be derived from aromatic compounds of non-combusted origin (e.g. lignin). BPCAs in the vials were dried under a gentle stream of ultra-high purity nitrogen on a heating plate (70°C) for 3 hours, and stored at -25°C until wet-oxidation to $CO_2$ gas for isotopic analyses [31,58] .

**Radiocarbon analysis**

BPCAs were converted to $CO_2$ using the wet oxidation procedure [29,31,58] for $\Delta^{14}C$ measurement using a gas ion source AMS. Following Lang et al., (2013) [60] and Wiedemeier et al. (2016)[29], 30 µg C samples and 4 ml of purified sodium persulfate were transferred to gas-tight borosilicate Exetainer vials, purged with ultra-high purity

helium (100 ml $min^{-1}$, 8 min), and oxidized to $CO_2$ in a heating block (95°C, 1 hr). Radiocarbon measurements were made on the Mini Carbon Dating System (MICADAS) Accelerator Mass Spectrometer coupled to a carbonate system modified with a needle to sparge sample solutions at the ETH Zurich Ion Beam Laboratory. Radiocarbon-depleted ($F^{14}C$=0.003±0.001) and modern ($F^{14}C$=1.149±0.004) wood char standards were used to evaluate the extraneous, or blank carbon added to samples during chemical processing [60,61]. PBC samples were corrected for extraneous carbon [58,61]. Radiocarbon is reported in $F^{14}C$ then converted to $\Delta^{14}C$ (‰) using the year of sampling.

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